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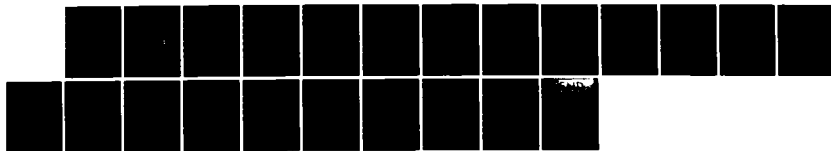
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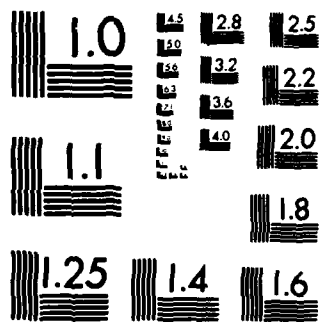
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20. ABSTRACT CONTINUED:

1.) Precursor formation - gas phase chemistry.

2.) Chemical nucleation - particle inception.

3.) Growth.

4.) Agglomeration, coagulation, and aggregation.

5.) Oxidation - competitive with each of the above.

The soot workshop topics were organized along the lines of the above list, with the significant addition of another category entitled Global Mechanisms and Mechanistic Limitations, which was the "catch-all" area.

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AeroChem TP-445

September 1984

THE MECHANISM OF SOOT FORMATION

A WORKSHOP HELD
14, 15 JUNE 1984

AT

AEROChem RESEARCH LABORATORIES, INC.
Princeton, NJ 08542

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INTRODUCTION

This report summarizes the presentations and discussions at an informal workshop on the mechanism of soot formation, held at AeroChem Research Laboratories, Inc. on the 14th and 15th of June 1984. The objective of this workshop was to assemble a few people who are concerned with the fundamentals of soot formation for a free exchange of information and stimulating discussions. This was intended to clarify the current state of understanding of the mechanism of soot formation and to inspire renewed efforts. We believe that these objectives were achieved. The attendees of the workshop are listed in Appendix I.

This report is AeroChem's summary of the presentations and discussions at the workshop. To assist the reader we have added some selected references. To minimize any bias that this report might convey, each participant was given an opportunity to review it in draft form and many of them suggested changes which have been incorporated herein. They were also invited to contribute brief comments which were to be included as Appendix II; no comments were obtained. The workshop was informal and organized to maximize discussions, so every effort was made to encourage productive discussions rather than the more frequently encountered "Sorry to interrupt this discussion, but we have to move on to the next speaker." Each person who reported on his current work chaired the ensuing discussions, with little or no "official" schedule.

Soot formation in pyrolysis and combustion involves complex reaction systems with many species and individual reactions. It also involves the transition of a gaseous chemical system into a particle-containing (i.e., two-phase) system. Thus, there are various stages of the soot formation process on which to concentrate research investigations. These are generally accepted to be:

1. Precursor formation - gas phase chemistry
2. Chemical nucleation - particle inception
3. Growth
4. Agglomeration, coagulation, and aggregation
5. Oxidation - competitive with each of the above

The soot workshop topics were organized along the lines of the above list, with the significant addition of another category entitled Global Mechanisms and Mechanistic Limitations, which was the "catch-all" area. The summaries below also follow this basic outline, with discussions reordered by topic rather than their actual sequence during the workshop.

PRECURSOR FORMATION AND NUCLEATION

PYROLYSIS SYSTEMS

Frenklach (Louisiana State University), the first speaker, gave an overview of the kinetic modeling of soot formation chemistry in the shock tube pyrolysis of acetylene,¹ work which has been performed jointly at LSU (Frenklach and Clary), University of Texas (Gardiner), and NBS (Stein). Their mechanism of about 600 reactions of 180 species consists of three parts: acetylene pyrolysis; formation of larger molecules and radicals; and further growth of aromatic rings. The model was used to compute simulations of soot produced in their shock tube experiments as a function of temperature. The main reaction bottleneck was found to be the formation of the first aromatic ring, for which 26 different pathways were considered. The analysis of these reaction steps was discussed in some detail by Frenklach. Both thermochemistry and kinetics were found to be important. Two rate limiting steps in the dominant process which produces the single ring aromatics are:



The formation of two-ring species was also found to be dominated by a single reaction pathway (from 10 pathways considered) of the two-step addition of acetylene to phenyl radical forming the naphthyl radical. An alternate route previously suggested by Bittner and Howard² was found to be minor. The mechanism considered further growth of species to large molecules which were expected to absorb 3.39 μm He-Ne laser light, and compared to experimental results. In either case, general bell-shaped soot yield vs. temperature curves were obtained in good qualitative agreement with experiment. The explanation of the shape of the bell curve was that at lower temperatures the pyrolysis kinetics limit the soot yield but these rates increase with temperature, until finally, at higher temperatures, the decreasing thermodynamic stability of the aromatic intermediates limits and ultimately decreases the yield.

Discussion of this work centered around the reaction chemistry of the first aromatic ring formation. Frenklach et al. estimated the rate coefficient of the bottleneck step, $C_4H_3 + C_2H_2$, to be $k = 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value of the rate constant was debated as possibly too high due to entropy effects in this combination reaction. The lifetime of the nascent C_6H_3 species was also questioned. Frenklach said that an order of magnitude lower rate coefficient would not change their conclusions. Calcote asked why ion-molecule reactions, which might be faster, were not considered for the bottleneck reactions, and Frenklach replied that they began by simply extending established mechanisms for major pyrolysis reactions in flames. He also noted that the source of $C_3H_3^+$ is unknown.

The chemistry of the second ring formation in this mechanism is also similar to that proposed by Bockhorn and coworkers³ in Darmstadt (W. Germany). The general mechanism involves cyclization by radical attack on an adjacent triple bond. Reactivity of intermediates is maintained through abstraction reactions. Frenklach et al. used this mechanism to describe further growth to larger species.

The reader is reminded that equally significant work is also being done on hydrocarbon flame reaction mechanisms relevant to the mechanism of soot formation by people who were not represented at this workshop; see, e.g., Refs. 4

and 5. Warnatz in a recent review⁴ states, "However, the explanation of the consumption of acetylene and the formation of higher hydrocarbons is rather difficult because of lack of detailed experimental information about the elementary reactions involved in the process."

Kern (University of New Orleans) discussed his recent work⁶ on aromatic hydrocarbon pyrolysis and soot precursor (building blocks) formation, which has been performed as a collaborative effort with other DOE supported workers (Skinner and coworkers at Wright State University, and Kiefer and coworkers at University of Illinois at Chicago). The three different shock tube diagnostic techniques in the three laboratories have identified and measured the rate parameters for the three main initial reactions in benzene pyrolysis (benzene decomposition into $C_4H_4 + C_2H_2$ and into $C_6H_5 + H$, and the decomposition of C_6H_5). Modeling studies using a mechanism comprised of the reaction chemistry for acetylene pyrolysis plus ten reactions for benzene and the chemistry of benzene's decomposition product showed good comparisons with the measured product species profiles. This mechanism supports the experimentally observed absence (small concentrations) of C_6H_5 in the mass spectrometric studies of benzene pyrolysis at temperatures greater than 1900 K, since the main products of the benzene decomposition are C_2H_2 and C_4H_2 .

Other work on toluene decomposition was also discussed. The initial decomposition rate coefficient of $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$ has been found by Skinner and coworkers⁷ to be 26 times lower than previously reported by Troe and coworkers,⁸ a significant finding. This disagreement has required reconsideration of the toluene reaction mechanism. In addition, the mechanism for ethylbenzene decomposition proposed by Troe and coworkers (to styrene + H) was questioned, with Kern favoring C-C bond cleavage. Mallard (National Bureau of Standards), indicated that Stein's (NBS) thermochemical calculations also support the proposal presented by Kern.

The soot (or PCAH) yield vs. temperature curves are always made using initial, not reaction shock temperatures. In Kern's simulation studies, this temperature differs significantly from the temperature at 1.5 ms, for example. Kern's calculated results show markedly decreasing temperatures with increasing observation time as the pyrolysis proceeds. He contends that soot yield data should be reported at the temperature corresponding to the chosen observation time (e.g., 1.5 ms) instead of the temperature calculated at time zero which is the common practice. Mallard and Frenklach postulated that the initial temperature probably controls the precursor chemistry.

Frenklach proposed that the magnitude of the temperature decrease in Kern's simulations has been overestimated since the mechanism did not contain a detailed description of soot formation (or higher molecular weight species). Frenklach reported that his computations indicated, for both the C_2H_2 and C_6H_6 cases, that soot formation is a highly exothermic process. The energy released in this process offsets the endothermicity of the initial phase.

These studies indicate that detailed reaction mechanisms with which to accurately simulate the pyrolysis of these small aromatic hydrocarbons, are now available and thus furnish concentration profiles of many decomposition products and reaction intermediates which may be relevant to soot precursor formation. However, the noted difficulty in fitting H-atom profiles with mechanisms (Kern) points out potential problems in making quantitative predictions which may strongly depend on the concentration of such reactive species.

Mallard presented a brief discussion of Stein's thermochemical work on the stability and reactivity of large aromatic molecules. Two main results are that (i) the reactivity per carbon atom of large PCAH molecules increases with molecule size, and (ii) there are identifiable "islands of stability," i.e., (for various carbon and hydrogen numbers), there are more stable structures which shift with temperature. At low temperatures (ca. 1700 K) there are no thermodynamic barriers, and at higher temperatures (ca. 2100 K), these barriers result in bottlenecks for the formation of larger and larger molecules. This observation may explain the bell-shaped soot yield (or PCAH yield) curves from fuel pyrolysis studies in shock tubes. This explanation appears to be in agreement with that discussed by Frenklach et al.

Mallard and coworkers also reported on work⁹ evaluating the possibility that "physical nucleation" of PCAH molecules produces soot. They calculated van der Waals dimer and trimer formation at 1400 K using example molecules with 1, 7, and 19 aromatic rings (benzene, coronene, and circumcoronene) and initial monomer concentrations based on, or larger than, observed concentrations in a turbulent diffusion flame. In no case could this route produce cluster concentration anywhere near the observed or estimated small particle concentrations. All polymers were concluded to occur at lower concentrations than the dimer. An unexpected result was that the calculated configuration of the clusters was not parallel, plane-to-plane, as one might expect. For example, the benzene dimer calculated to be most stable contains two molecules in a perpendicular configuration. Thus, physical nucleation seems to be ruled out. He, however, pointed out that physical clustering of charged PCAH ions might be faster and the clusters more stable.

There appeared to be agreement that neutral, physical nucleation is unlikely to be important in soot formation. Continued growth from small molecules to very large "particle-like" molecules with no discrete "nucleation" point represents the general viewpoint of the audience. This is sometimes called "chemical nucleation."¹⁰

COMBUSTION SYSTEMS

Eyler (University of Florida) discussed his work using ion cyclotron resonance and Fourier transform mass spectrometers¹¹ to measure the near room temperature reaction rate coefficients of $C_3H_3^+$ with various neutral species, similar to previous work performed at NBS by Ausloos and coworkers. As found before, there are large differences in reactivity between the linear, more reactive $C_3H_3^+$ and the cyclic, more stable isomer. Numerical results were presented for reactions of both isomers with several hydrocarbon, including oxygen-containing, molecules. In many cases the cyclic $C_3H_3^+$ is nonreactive, but it often has a smaller, but still significant, reaction rate coefficient compared with the linear form. Some of Eyler's work indicates that the linear $C_3H_3^+$ was produced with excess internal energy, possibly 0.5 eV (48 kJ mol⁻¹). The possibility that this might complicate the kinetic results was discussed, but Eyler cited their similar experiments using an ion source that didn't result in $C_3H_3^+$ with excess energy. Overall, these results show that these ion-molecule rate coefficients are fast to moderately fast, and that they decrease somewhat with increasing size for larger aromatic molecules (e.g., toluene, indene, methyl-naphthalene). This decrease in rate coefficients for larger molecules could complicate the ion-molecule mechanism for soot formation. However, Eyler

suggested that ion-molecule reactions could be important in certain portions of the overall reaction mechanism and neutral chemistry could dominate other portions with possible switching between these two parallel pathways!

A major unresolved problem is the form of the $C_3H_3^+$ ion observed in flames. The role of the reactivity of linear $C_3H_3^+$ was questioned since the cyclic structure is more stable by about 1 eV and (presumably) is the more likely isomer in flames. Since the mechanism for its formation is not known, the energy (or form) of the nascent ion cannot be predicted. Calcote (AeroChem) noted that rapid equilibrium could maintain the linear form at fairly high concentrations in either case. Several experimental methods for determining the form of the $C_3H_3^+$ ion by measuring its reactivity either in situ or after molecular beam sampling were suggested. It was agreed that any of the proposed methods would be difficult.

The discussion continued on the role of ions in various soot producing environments.

Santoro (NBS) asked Calcote the temperature at which he would expect chemi-ions to be formed. The reply was that they can appear at any temperature since their formation (CHO^+) is a nonequilibrium process which always occurs in the presence of CH and O. When these species were produced in a room temperature flow tube, for example, chemi-ions were produced.

The significant question of whether chemi-ions can be produced in fuel pyrolysis systems, such as shock tube hydrocarbon decomposition experiments which produce soot, was raised. The mechanism by which $C_3H_3^+$ would be produced in such systems is not clear. Calcote noted that only a few experiments have been performed to measure ion production in pyrolysis systems,^{12,13} but that in every case the experimental result confirmed their production. This previous work was not definitive, because oxygen could have been present as an impurity. Lester (LSU) discussed his shock tube work of several years ago in which he observed unexpected probe currents in C_2H_4/Ar pyrolysis between 1400 and 2000 K, and said that he worked several months to remove what he initially thought was an experimental artifact. He could not eliminate the currents, and thus concluded that ions were being formed. He also observed CH^* light emission.

Santoro commented that he had seen a proposed reaction mechanism and first steps in quantitative simulations of soot formation in pyrolysis systems using neutral/free radical reactions, but none for the ion-molecule mechanism. Olson (AeroChem) replied by showing results¹⁴ of a simulation of an acetylene/oxygen flame which included the normal combustion mechanism plus a simplified set of ion-molecule reactions. The resulting concentration profiles showed reasonable qualitative comparison with experiments. Olson, however, called this work much less complete and quantitative than the work of Frenklach et al.

Calcote presented an overview of the AeroChem work¹⁵ on the ionic theory of soot formation in low pressure sooting flames. A schematic mechanism was presented which begins with $C_3H_3^+$ and, through sequential addition of C_2H_2 , produces large aromatic ions. All of the species in the mechanism are observed in sooting flames and all of the reactions are exothermic so should have large rate constants. An extensive plot of concentration vs. time for the well-studied low pressure C_2H_2/O_2 flat flame, which combines data from AeroChem (Calcote and coworkers), MIT (Howard and coworkers), German studies (Homann, Wagner, and

coworkers), and French studies (Delfau and coworkers) was discussed. Calcote pointed out the advantage of different groups working in similar flame systems in order to produce more complete data sets with which to evaluate soot formation mechanisms. The chemi-ions in this model flame reach a maximum concentration early in the flame, and decay as the soot particle number density increases. A sufficient number of ions is observed to account for the soot particles. Positive ion recombination rate coefficients, measured in fuel-rich and sooting flames, show a major change at the soot threshold which is consistent with an increase in positive ion size and the hypothesis that significant electron attachment to particles occurs.

Characteristic times were used to compare the estimated rates of various neutral and ionic processes in the model flame at two positions using measured concentration data from the flame. Many processes can be deemed unimportant in soot nucleation when their rates are much slower than the characteristic flow time in the flame. For repeating steps, such as the addition of C_2H_2 to a growing ion, about 10^3 steps are required, so the characteristic time must be shorter than 10^{-3} times the characteristic flow time. The proposed ionic steps satisfy this criteria even when a T^{-2} temperature dependence is imposed on the Langevin rates.

The discussions focused on several questions. Mallard suggested that rate coefficients for growth of large ions should be smaller than for small ions. Eyler said that, theoretically, ion-molecule rate constants do not necessarily decrease with increasing temperature or size. Calcote stated that ion-molecule reactions are known to be fast in high temperature stoichiometric flames. The question of pyrolysis systems was raised by Frenklach, who wondered how an ionic mechanism could describe the bell-shaped soot yield temperature dependence from shock tube experiments. Calcote drew parallels with the thermochemical limitations for the stability of ions as previously discussed for neutral species. Harris (GM Research Laboratories) added that a composite ionic-neutral radical mechanism (such as that suggested by Eyler) could show the same behavior due simply to instability in the radical part of the soot formation.

Asked about the rates of ion formation in pyrolysis systems, Calcote said he was not even sure what they are in rich flames. Frenklach suggested that if addition of some O_2 to acetylene in shock tube pyrolysis produces more ions, then the observation of lower soot production could vitiate the importance of ions in soot formation. Calcote point out the need for quantitative data and analysis to evaluate this question; at this time the ion formation rates in fuel rich flames, much less in pyrolysis systems, are not known.

Harris presented results¹⁶ from a series of experiments in which he compared soot volume fractions, number densities, temperatures, and surface growth rates from an atmospheric pressure premixed $C_2H_4/O_2/Ar$ flame (the base flame), and two higher C/O flames, obtained by adding a small increment of C_2H_4 to the base flame or by adding an equivalent amount of carbon in the form of toluene to the base flame. Although the acetylene, benzene, and toluene concentrations in the burned gases were different in the two flames with added fuel, the soot surface growth constant, number density, and volume fraction were the same. He concluded that addition of C_2H_4 or C_6H_6 to the base flame produced the same increase in soot per carbon added. Since the concentration of benzene and toluene in the particle inception zone changed by a combined factor of 3.5, it was deduced that particle inception in these flames did not depend on the concentration of benzene and toluene. Most of the original fuel molecules are fragmented

and lose their original identity. There was general agreement that in premixed flames most of the fuel breaks down into small fragments which then undergo a similar soot formation route regardless of the original fuel structure.

There was some general discussion of cause and effect in correlations of sooting with aromatic character of intermediate molecules. Glassman (Princeton University) suggested¹⁷ that in premixed flames the correlation is through OH concentration and OH attack on the original fuel and hydrocarbon intermediates. In diffusion flames, he pointed out, the fuel molecules can survive long enough to affect the sooting process. Kern and Frenklach cited the importance of aromatic rings in soot formation in pyrolysis systems. Yet Harris pointed out that his work showed that not all of the aromatic molecules are broken down in these flames, and that there is no evidence that they play any part in the soot formation process at all when present at the low concentrations studied. Since soot is only observed after surface growth by C_2H_2 addition to the initial particles, we do not know either the initial species or its structure. Conceivably, it may not even have been a PCAH as generally assumed. Harris posed the possibility that some of the PCAH observed after surface growth may have formed on the soot surface. This could also explain, in principle, the correlation between PAH and soot. Or, there could be no cause and effect relationship at all.

Mallard expressed some concern that the small difference (a factor of two) in benzene concentrations between the flames was insufficient evidence on which to base the lack of correlation, and also that the relative time origin (located at about the beginning of the soot containing region) made the data slightly confusing. Harris replied that the aromatic concentration differences were experimentally significant and that the conclusions were not altered by any reasonable shifting of the time axis.

Glassman commented that he would not expect addition of carbon to the flame in the form of CH_4 to produce the same result as addition of toluene. Harris responded that experiments by Haynes et al.¹⁸ confirmed that CH_4 addition produces an equivalent increase of soot per carbon atom, consistent with his view that in the fuel breakdown, the available carbon is the important parameter controlling the soot yield for premixed flames made up primarily from ethylene. Harris acknowledged that CH_4 addition to the ethylene flame would also change the C/H ratio, which could make a difference, although small increments of CH_4 should have little effect on the overall C/H ratio.

SOOT SURFACE GROWTH

Harris also compared his rate equation¹⁹ for soot mass growth, $dM/dt = k_1(\text{Surface Area})(C_2H_2)$, where k_1 has been found to decay with the "age" of the soot particles, with the Haynes and Wagner²⁰ formulation of soot growth, $dM/dt = k_{sg}(M^* - M)$, where, in both cases, M is the total mass of soot and in the latter equation M^* is the final value of M . Dasch²¹ (GM Research Labs.) has shown that the two formulations are actually equivalent, and that Haynes and Wagner's k_{sg} is the inverse of the time constant for the decay of the Harris and Weiner k_1 and not a rate constant for surface growth. The value of the Haynes and Wagner k_{sg} is independent of time and soot surface area, but is temperature dependent, as would be expected for a time constant for decay of soot reactivity.

Harris showed an Arrhenius plot due to Dasch²¹ for the reaction probability of C_2H_2 on carbon, which spanned a wide range of temperatures. The decay of reaction probability for soot particles with age is only qualitatively understood.

There appeared to be general acceptance of Harris's description of soot surface growth in premixed flames

AGGLOMERATION, COAGULATION, AND AGGREGATION

This area of soot formation did not spark much discussion. Harris showed data on soot particle number densities from his flames and on calculated profiles using a time origin estimated for the end of the nucleation processes. Data and theory are in good agreement. The initial number density of particles does not determine the number density of particles downstream since the higher the initial number density the faster the particles coagulate, which always results in consistent numbers of particles. However, the initial number density does affect the size of the particles. Thus, a higher nucleation rate leads to particles with more surface area, which therefore have more surface growth. In this way, the number of incipient particles controls the ultimate volume fraction even though it has no effect on the final number density.

SOOT OXIDATION

Olson presented a brief overview of a new program in which he (with Felder and Madronich, AeroChem) is measuring carbon black and soot particle oxidation by O_2 , CO_2 , and H_2O in a high temperature fast flow reactor, HTFFR. Although O atoms and OH are efficient oxidizers of soot, in many applications such as engines which operate with excess air, the overall rate of soot oxidation is due to both OH and O_2 attack. The low concentration of O atoms precludes their importance in almost all applications. The flow tube technique will make a wider range of temperature, time, and reagent concentration conditions accessible than previously studied, and will allow measurements where the reaction is kinetically rather than diffusively controlled.

In his measurements Harris sees O_2 surviving into and just past the nucleation zone in superequilibrium concentrations, and thus possibly contributing more to soot oxidation than previously estimated. He also mentioned some work in the Russian literature by Tesner which might be of interest.

GLOBAL MECHANISMS AND MECHANISTIC LIMITATIONS

Glassman presented an overview of the Princeton work on premixed¹⁷ and diffusion flame²² sooting tendencies, and emphasized the different dominant processes in each which result in different temperature dependencies. Raising the flame temperature in diffusion flames increases the rate of fuel pyrolysis and thus increases the amount of soot formed; whereas higher premixed flame temperatures increase the precursor oxidation rate faster than the soot production rate, and thus reduce the premixed flame's tendency to soot. He described

their correlation¹⁷ of constant temperature premixed flame soot thresholds (using dilution to adjust the flame temperature as calculated via an adiabatic assumption) vs. C-C bond number. The good correlation of this plot was interpreted to mean that all fuels break down into the same fragments and then build up to soot. A comparison was made with the diffusion flame, in which the soot forms and grows in the fuel pyrolysis zone, where the fuel structure affects the soot formation processes. The importance of the OH concentration in premixed flames was mentioned. Glassman did not identify the vital precursor for soot, but he eliminated acetylene.

Harris mentioned results of Cole et al.²³ which showed that different fuels at the same C/O ratio (in premixed flames) produced different quantities of products and intermediates, such as PCAHs and C_2H_2 . Several people stressed the difference between soot yields and soot thresholds (or sooting tendencies). Glassman argued that Harris's work shows that in premixed flames the ultimate amount of soot depends on the processes leading to the nucleation process; thus the soot threshold should correlate with the soot yield for various fuels. He dismissed the observed differences in correlations as temperature effects. Lester and Harris asked why several fuels exhibit the same qualitative sooting tendency in shock tubes and in diffusion flames. Glassman countered that in both systems the soot formation was controlled by fuel pyrolysis alone and the ability of the fuel to form the precursors for soot nucleation.

Santoro cautioned about using calculated temperatures for these comparisons since the addition of N_2 to a diffusion flame reduces the calculated temperature but has been observed to raise the measured temperature near the flame tip, because less soot remains in the flame and therefore the radiative heat losses are smaller. Glassman argued that in the Princeton work the calculated adiabatic temperatures should scale with the true temperatures, assuming roughly constant temperature profiles (i.e., similar flow profiles and radiative losses), and suggested these calculated temperatures might be called "surrogate temperatures."

Glassman also mentioned some work showing that small additions of methyl-naphthalenes to flames greatly increase their luminosities. Lezberg (NASA-Lewis) confirmed this for soot yields in combustors. Olson pointed out that AeroChem has developed²⁴ rules for calculating the soot thresholds for multicomponent fuel mixtures in both premixed and diffusion flames which accurately describe the addition of small (or large) amounts of very sooty components to other fuels.

Calcote discussed the desirability of assuming combustion products in premixed flames of $CO + H_2O$ (as suggested by Glassman) instead of $CO_2 + H_2O$ or other combinations of $CO/CO_2/H_2/H_2O$. Equilibrium compositions of the combustion products at the observed soot thresholds of a series of fuels, plotted against soot threshold, show²⁵ a linear shift in composition. That is, low sooting fuels actually produce mostly CO but fuels with higher tendencies to soot, e.g., aromatic fuels, produce a mixture of CO and CO_2 . These calculations show a mixture of H_2 and H_2O is produced for all fuels. Thus, no single assumption about the combustion products is correct for a series of fuels with different tendencies to soot.

Olson reported on the soot threshold, soot yield, and flame temperature measurements that they have made in premixed flames²⁵ (55 fuels) and in diffusion flames²⁶ (42 fuels). These data have been reported in the form of threshold soot indices, TSIs, which allow these results to be combined with other data from

the literature, and give measured soot thresholds for a total of 73 fuels in premixed flames and 103 fuels in diffusion flames. The study of so many fuels facilitates calculations of the soot thresholds of practical multicomponent fuels from knowledge of their composition and the characteristics of their components. Mixture rules which allow this procedure to be followed quantitatively for both diffusion and premixed flames were discussed.²⁴ In answer to a question, he said that the mixture rules can quantitatively explain the large effect of methylnaphthalene addition on flame luminosities.

Olson showed soot yield curves for several fuels in premixed flames, which have been parameterized by fitting to an exponential form: $f_v = A_i \exp(B_i \phi)$, where the A_i and B_i are characteristic of individual fuels. He said these had been measured for about 40 fuels.

Other data were presented for decalin and toluene premixed flames where the $O_2/(N_2 + O_2)$ ratio was varied to shift the soot thresholds. Although the observed soot threshold equivalence ratios shifted with N_2 dilution as expected, measurements using two-wavelength emission pyrometry showed the soot threshold temperature to be the same for each fuel (1750 K for toluene and 1720 K for decalin), independent of the dilution and soot threshold equivalence ratio. This result was surprising since the calculated adiabatic temperatures showed a slope of soot threshold vs. (calculated) temperature, whereas the measured temperatures showed no difference. Various experimental details were discussed but no plausible explanation was found in the experimental technique. The effect of flow velocity on the soot thresholds was not known, and it was suggested that it be investigated.

Further results presented from these same two flames, on soot concentrations at various equivalence ratios and dilutions in sooting flames, showed all of the data from each fuel coalesced onto a single $\log f_v$ vs. $1/T$ curve. These results were reported to be the first data of this type to be measured. Thus it appears that the soot yield for a particular fuel is simply a function of flame temperature under these conditions.

Santoro discussed his work²⁷ on cylindrical C_2H_4 /air diffusion flames, which includes measurements of soot particle size, number densities, volume fractions, flow maps, and temperatures. Generally, near the base of the flame the particles are observed to be formed slightly inside, on the fuel side of the reaction zone. There is much molecular scattering and fluorescence, but the particle scattering has been identified. According to Santoro the molecular scattering precedes the soot particles and the fluorescence acts as a "marker" for the particles. Mallard reported finding small particles (≈ 2 nm), as detected by laser ionization, appearing after the fluorescence. Santoro thinks the fluorescent region is located at the start of the soot formation zone. Mallard then commented that the fluorescence intensity (probably from PCAH) in diffusion flames parallels the sooting tendencies for a few fuels. Harris suggested that although they were correlated through similar chemistry, they may not be related through cause and effect.

In the center of his flame, Santoro observed soot where the temperature had reached 1350 K (uncorrected thermocouple temperature). Near the reaction zone, particle inception occurs in about 20 ms, while near the flame axis, particles were observed only after about 60 ms, probably due to the lower temperatures on axis. Examining preliminary data on the nucleation rates, Santoro

found a particle production region extending from the primary reaction zone near the base of the flame into the core of the flame at higher positions.

Sidebotham (Princeton University) asked if there was a characteristic soot formation time or temperature, but Santoro said he had not found a simple, single relationship in the data. Glassman asked if there were any oxygenated species in the region of particle formation, and Santoro said yes, probably about a percent.

Soot volume fractions were compared for several flames. Santoro observed that the fuel CH_4 gave about the same yield as a $\text{C}_2\text{H}_4/\text{N}_2$ mixture which would have about the same calculated adiabatic temperature. He also pointed out that for two or three fuels tested, they always observe the same size particles regardless of the conditions. He discounted the importance of diffusion of particles into the inner flame regions.

Flower (Sandia National Laboratories) discussed his work²⁸ on Wolfhard-Parker type C_2H_4 /air diffusion flames at elevated pressures from 1 to 2.5 atm. Higher pressure flames exhibit higher soot concentrations with about a $P^{1.5}$ to $P^{2.0}$ dependence. The soot increase is found to be attributable to both higher number densities and larger particles. Measured maximum flame temperatures decrease by about 100 K between 1 to 2 atm, even though the equilibrium adiabatic flame temperature increases. Increased radiative heat losses due to higher soot concentrations probably explain this temperature behavior. Glassman asked how increased sooting could reduce temperature yet continue to promote increased soot formation, when pyrolysis (which is important for sooting) increases with temperature. Santoro rationalized this in terms of the sequence: pyrolysis, soot formation, cooling, followed by oxidation, leading to less interaction between nuclei formation and soot cooling than in premixed flames.

The effects of buoyancy on these flames at various pressures was discussed, but there was no general agreement.

Some interesting preliminary data on the flame transmission at 515 nm showed an unusual intermediate absorption zone at higher pressures between the burner axis and the flame zone. No explanation was available for this observation.

Calcote introduced the question of whether the soot formation mechanism is the same in premixed flames, diffusion flames, pyrolysis systems, and turbulent flames. The discussion divided the group into two camps: those who consider a large reaction mechanism to be the same when applied to different systems with different temperatures, reagent concentrations, gas dynamics, etc. and who hold that the mechanism naturally shifts with these conditions to make different reactions dominant under different sets of conditions; and those to whom these shifts in dominant individual reactions under various conditions indicate that the mechanisms are different. For example, to the latter group, diffusion flames have a different sooting mechanism from premixed flames, whereas to the first group, the lower temperatures and higher fuel concentrations in areas of diffusion flames simply shift the part of the mechanism controlling the final result. Actually everyone seemed to be saying the same thing, just in different ways.

However, Calcote pointed out that there may be different sooting mechanisms in turbulent flames but too little work has been done on sooting tendencies of fuels in turbulent flames. Tishkoff (AFOSR) suggested, from a fluid dynamicist's point of view, that all try to broaden their knowledge to include other fields which encompass the physical phenomena that they study. Some of this other work is relevant to the soot formation problem.

Glassman said that, in a practical sense, there is an important difference between diffusion and premixed flames, especially in the dominance of pyrolysis and soot particle oxidation processes in diffusion flames. Lezberg questioned the study of soot formation in diffusion flames, since the system is much more complicated than shock tubes or premixed flames and therefore harder to understand. Santoro pointed out that the very complexity and dominance of pyrolysis and soot particle oxidative processes in diffusion flames makes their study more applicable to practical combustors and fires, even though it also makes their study more difficult.

CONCLUSIONS

Recent work has significantly advanced the understanding of the mechanism of soot formation in pyrolysis and combustion systems. Detailed kinetic mechanisms are now being successfully tested for the pyrolysis of aromatic hydrocarbons and should soon improve those used for fuel-rich combustion modeling. The work by Frenklach and coworkers is a pioneering step toward finally being able to computer simulate the soot formation process, including a free radical ring closing step, and therefore being able to test the relevance of proposed chemical and thermodynamic processes. The chemical nucleation step remains the least understood.

What are some important unsolved problems in soot formation?

I. Fundamental Mechanism

1. Is the formation of a ring structure early in the soot growth process important (it is usually considered so)?
2. Is the formation of the first or second aromatic ring due to a free radical or an ionic reaction?
3. What is the role of PCAHs in soot formation? Are they a cause, result, or a side product?
4. Is the basic mechanism, e.g., precursor formation, ring closure, and growth the same in pyrolysis, premixed, and diffusion flames, i.e., can a single reaction path be used to describe all three systems recognizing varying significance of specific steps in the three systems?

To answer these questions work is required on:

1. Measurement or more accurate calculation of the rate coefficient of the key reaction steps, especially at flame temperatures.

2. An increased thermodynamic data base, especially for large species.
3. Computer simulations of reacting systems for both free radical and ionic systems.
4. Detailed measurements characterizing pyrolysis, premixed flames, and diffusion flames, and especially measurements of concentration profiles of the species considered in the mechanisms and particularly in diffusion flames.
5. The rate of ion formation in fuel-rich flames.
6. Ionization in pyrolysis systems.

II. Phenomenonological Information Important to Mechanism Considerations

What is the role of:

1. Temperature
2. Pressure
3. Fuel Mixtures
4. Chemical Additives
5. Turbulence
6. Particle and Precursor Oxidation Processes

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